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Relative Stabilities of Tetramethyl Orthosilicate  
and Tetraethyl Orthosilicate in the Gas Phase

by

Jason C. S. Chu, James Breslin,  
N. S. Wang and M. C. Lin

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Relative Stabilities of Tetramethyl Orthosilicate  
and Tetraethyl Orthosilicate in the Gas Phase

Jason C. S. Chu, James Breslin,  
N. S. Wang<sup>#</sup> and M. C. Lin<sup>\*</sup>

Department of Chemistry  
Emory University  
Atlanta, GA 30322

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# Present address: Department of Applied Chemistry  
Chiao Tung University, Hsinchu, Taiwan

\* To whom correspondence should be addressed.

## **Abstract**

The stabilities of  $\text{Si}(\text{OCH}_3)_4$  and  $\text{Si}(\text{OC}_2\text{H}_5)_4$  have been studied pyrolytically using highly diluted mixtures near atmospheric pressure conditions. FTIR spectrometric analyses of the disappearance of the reactants and the formation of various major stable products allow us to qualitatively account for the global difference in the measured overall first-order decay constants:

$$k \text{ (TMOS)} = 1.4 \times 10^{16} \exp(-81,200/RT) \text{ s}^{-1}$$

$$k \text{ (TEOS)} = 7.4 \times 10^{10} \exp(-49,500/RT) \text{ s}^{-1}.$$

TMOS is significantly more stable than TEOS. The mechanistic implication of these results is discussed.

## 1. Introduction

The deposition of  $\text{SiO}_2$  as an insulating film is an important part of microelectronic fabrication process [1]. For the  $\text{SiO}_2$  film preparation, there have been attempts to replace the traditional dry oxidation and silane oxidation processes by silicon alkoxide CVD (chemical vapor deposition) [2,3]. Despite the growing interest in this OMCVD (organometallic CVD) process, the kinetics and mechanisms of the thermal decomposition of silicon alkoxides or tetra-alkyl orthosilicates,  $\text{Si}(\text{OR})_4$ , in the gas phase remain virtually unknown.

Because of the close coupling of the gas phase chemistry with surface reactions under normal atmospheric OMCVD conditions [4,5], it is of great importance that the kinetics as well as mechanisms of gas phase reactions be fully elucidated. For tetra-alkyl orthosilicates, the only gas-phase kinetic study, to our knowledge, was performed by Ivanov et al. [6] for tetraethyl orthosilicate, TEOS. The effective rate constant measured by a flow technique was reported to be  $k \approx 10^6 \exp(-20,000/RT) \text{ s}^{-1}$ , where  $R = 1.987 \text{ cal/mol.deg}$ .

In order to compare the thermal stabilities of tetramethyl orthosilicate, TMOS, and TEOS, we have recently carried out a series of experiments using highly diluted mixtures of these compounds near atmospheric - pressure conditions to minimize surface effects. The products of the decomposition reactions were analyzed by Fourier-Transform Infrared (FTIR) spectrometry. The results of this pyrolytic study indicates that TMOS is far more stable than TEOS. This preliminary result will be discussed in terms of their reaction mechanisms.

## 2. Experimental

The thermal decompositions of TMOS and TEOS were carried out in a 270 - ml quartz reactor heated with a double-walled cylindrical furane. The reactor temperature was controlled and measured to  $\pm 0.5$  K with a thermocouple placed in a small tube sealed at the center of the reactor employing a solid-state temperature controller (Omega CN-9000). The concentrations of the reactants were varied from 0.6 - 1.4% for TMOS and 0.06 - 0.30% for TEOS using argon as diluent. Pyrolysis was carried out between 858 and 968 K for TMOS and between 721 and 820 K for TEOS, providing a reasonable reaction period covering from several minutes to several hours. The reaction pressures for both systems were kept constant and maintained near atmospheric pressure to minimize reactor wall effects, which often alter not only the kinetics but also the mechanism of the initial, rate-controlling step.

Both pyrolyzed and unpyrolyze samples were analyzed by FTIR spectrometry with a Mattson Instrument Polaris spectrometer using a 15 cm long, 2.5 cm O.D. sample cell sealed with two KCl windows. The analysis cell was connected directly to reactor and the associated vacuum system, which could be evacuated to typically  $5 \times 10^{-5}$  torr before each run.

The reaction products identified in the TMOS decomposition by FTIR were CO, CH<sub>2</sub>O, CH<sub>3</sub>OH and CH<sub>4</sub>. A typical set of spectra for the pyrolyzed and unpyrolyzed samples of TMOS, is shown in Fig. 1. A similar set of results for TEOS is presented in Fig. 2. As indicated in the figure, the decomposition products identified in this system are: CO, C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>CHO and C<sub>2</sub>H<sub>5</sub>OH.

The concentrations of the major products identified in the thermal decomposition reactions were calibrated with more than 10 sets of mixtures composing of varying amounts of products. The pressures of the calibration

samples were always kept the same as those of the expanded, pyrolyzed or unpyrolyzed reaction mixtures, in the absorption cell. In this manner, the effect of pressure (or Lorentz) broadening can be properly corrected for. The concentrations of reactants and products were quantitatively analyzed with a multicomponent analysis program supplied by Mattson.

### 3. Results

Typical sets of concentration-time profiles measured for the TMOS and TEOS systems are presented in Figs. 3 and 4, respectively. The rates of disappearance of both compounds were, unexpectedly, found to be approximately first order as illustrated in Fig. 5. From the slopes of these first-order plots one can evaluate the apparent first-order rate constants for the disappearance of the two reactants:



It should be mentioned that because of the formation of small molecular products, such as CO, CH<sub>2</sub>O and CH<sub>4</sub>, it is expected that both reactants may have been consumed, at least in part, by radical attacks, as will be discussed later.

The rate constants presented in Fig. 6 can be effectively represented by

$$k_1 = 1.4 \times 10^{16} \exp(-81,200/RT) \text{ s}^{-1}$$

$$k_2 = 7.4 \times 10^{10} \exp(-49,500/RT) \text{ s}^{-1}$$

As is evident from above equations, the difference between these two systems in terms of both pre-exponential factor and activation energy is very significant. Overall, TMOS is significantly more stable thermally than TEOS. At 770 K, for example,  $k_1$  is 4 orders of magnitude smaller than  $k_2$ .

Inasmuch as the difference in the strengths of Si-O and O-C bonds in these two molecules is not expected to be large, the observed dramatic difference in stabilities must have resulted from the intrinsic mechanistic variance between these decomposition processes.

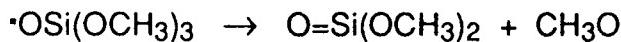
#### 4. Discussion

The significantly different Arrhenius parameters measured for the thermal decomposition of TMOS and TEOS suggest that the rate-controlling steps in these two systems are greatly different. For TMOS,  $A = 1.4 \times 10^{16} \text{ s}^{-1}$  reflects a very loose transition state, typical for a bond-breaking process producing radical products. The high activation energy, 81 kcal/mole is qualitatively in accord with such a bond-breaking process. Although the strengths of the C-O and Si-O bonds in TMOS are not known, the former is likely to be in the range of 80 - 85 kcal/mole, while the latter  $\geq 100$  kcal/mole [7].

Thus, the initial decomposition of TMOS is most likely

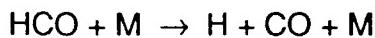
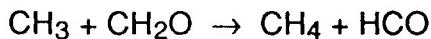
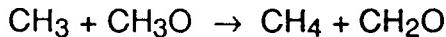


followed by a relatively short chain reactions. For example:



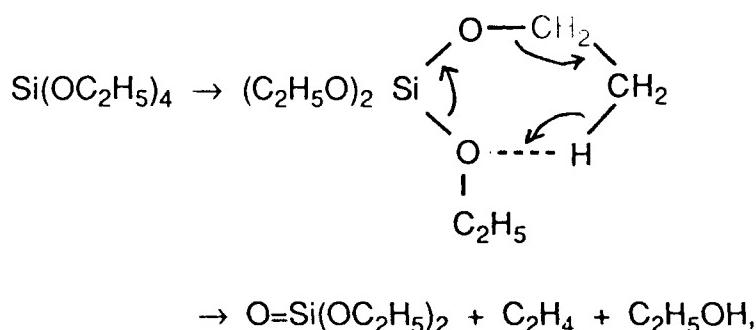
The O=Si(OCH<sub>3</sub>)<sub>2</sub> molecule is expected to be a key intermediate because its carbon analog, O=C(OCH<sub>3</sub>)<sub>2</sub>, (dimethyl carbonate) is a very stable, commercially available chemical.

The production of CH<sub>3</sub>O and CH<sub>3</sub> can account for the observation of CH<sub>4</sub>, CH<sub>2</sub>O and CO:

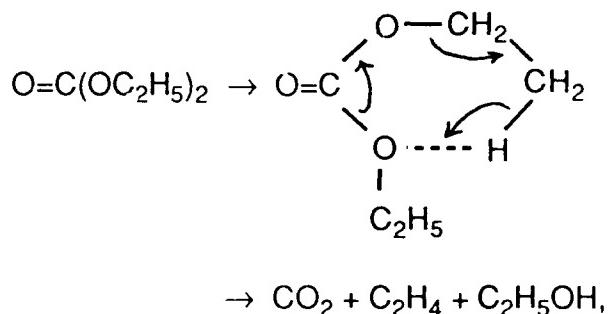


These radicals may also attack the parent TMOS molecule leading to the lowering of the activation energy. These subsequent radical reactions may in fact be unimportant; otherwise, TMOS decay would not obey the first-order rate-law and the A-factor for k<sub>1</sub> would be significantly lower-than 10<sup>16</sup> s<sup>-1</sup>. We hope to perform a rudimentary kinetic modeling to sort out the unimolecular decomposition kinetics in the near future.

Contrary to TMOS, the low A-factor and activation energy measured for TEOS suggest that the initial decomposition may occur by a rather tight, ring-complex, such as [6]

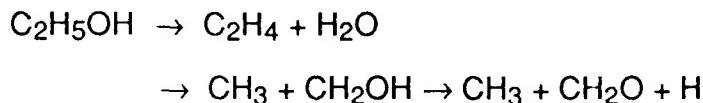


producing the stable molecular products as given. This mechanism is similar to the known 6-centered molecular decomposition process for the diethyl carbonate [8]:

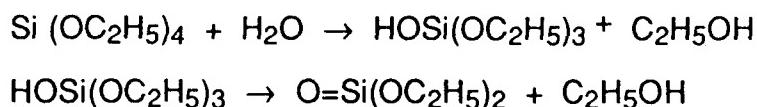


whose unimolecular decomposition constant has been measured to be k = 7 × 10<sup>13</sup> exp(-46,000/RT) s<sup>-1</sup>. A similar mechanism may indeed be responsible for the production of SiO<sub>2</sub> from O=Si(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, accompanying by the generation of additional C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>5</sub>OH.

Since C<sub>2</sub>H<sub>5</sub>OH is unstable under the conditions employed (T > 720 K, P = 760 torr), it may decompose thermally to produce:



The radical species thus formed may attack TEOS and all molecular products accumulated in the system to produce CO, CH<sub>4</sub> and CH<sub>3</sub>CHO, similar to those reactions presented above. Among these secondary products formed, H<sub>2</sub>O may have the most profound effect on the acceleration of TEOS decomposition via hydrolysis [9].



This catalytic process produces additional C<sub>2</sub>H<sub>5</sub>OH, which in turn generates more H<sub>2</sub>O. These secondary reactions, which are not present in the TMOS system, may account for the lowering of the A-factor from a typical value of  $5 \times 10^{13} - 1 \times 10^{14} \text{ s}^{-1}$  for a 6 - centered molecular elimination process [10] to  $7 \times 10^{10} \text{ s}^{-1}$  measured in the present experiment. With a low pressure flow method, Ivanov et al. obtained a value as low as  $10^6 \text{ s}^{-1}$  [6]. We hope to quantify the extent of the H<sub>2</sub>O catalysis effect by kinetic modeling.

### Acknowledgment

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### References

1. B. C. Rhine, Solid State Technology 32 (1989) 129.
2. A. C. Adams and C. D. Capio, J. Electro Chem. Soc. 126 (79), 1042.
3. S. Nguyen, D. Dobuzinsky, D. Harmon, R. Gleason, S. Fridmann, J. Electrochem. Soc. 137. (1990), 2209.
4. S. B. Desu, J. Am. Ceram. Soc. 72 (1989) 1615.
5. S. R. Kalidindi and S. B. Desu, J. Electrochem. Soc. 137 (1990) 624.
6. M. Ya Ivanov, T. N. Kupryashkina, V. Z. Kompaniets.  
M. A. Kopteva, A. A. Konoplev. Z. Prikladnoi. Khimii. 58 (1983) 1838.
7. T. L. Cottrell, "The strengths of chemical bonds." Academic Press. Inc.,

New York 1954.

8. A. S. Gordon and W. P. Norris, J. Phys. Chem. 69 (1965) 3013.
9. D. C. Bradley, Chem. Rev. 89 (1989) 1317.
10. S. W. Benson and H. E. O'Neal, Kinetic Data on Gas-Phase Unimolecular Reactions, NSRDS-NBS21, National Bureau of Standards, 1970.

Fig 1. Typical TMOS FTIR spectra from 207 torr samples. (A) 0.60% TMOS/Ar mixture pyrolyzed at  $P=705$  torr and  $T = 940$  K for 6 minutes. (B) unpyrolyzed 0.6% TMOS/Ar mixture (C) the difference between (A) and (B).

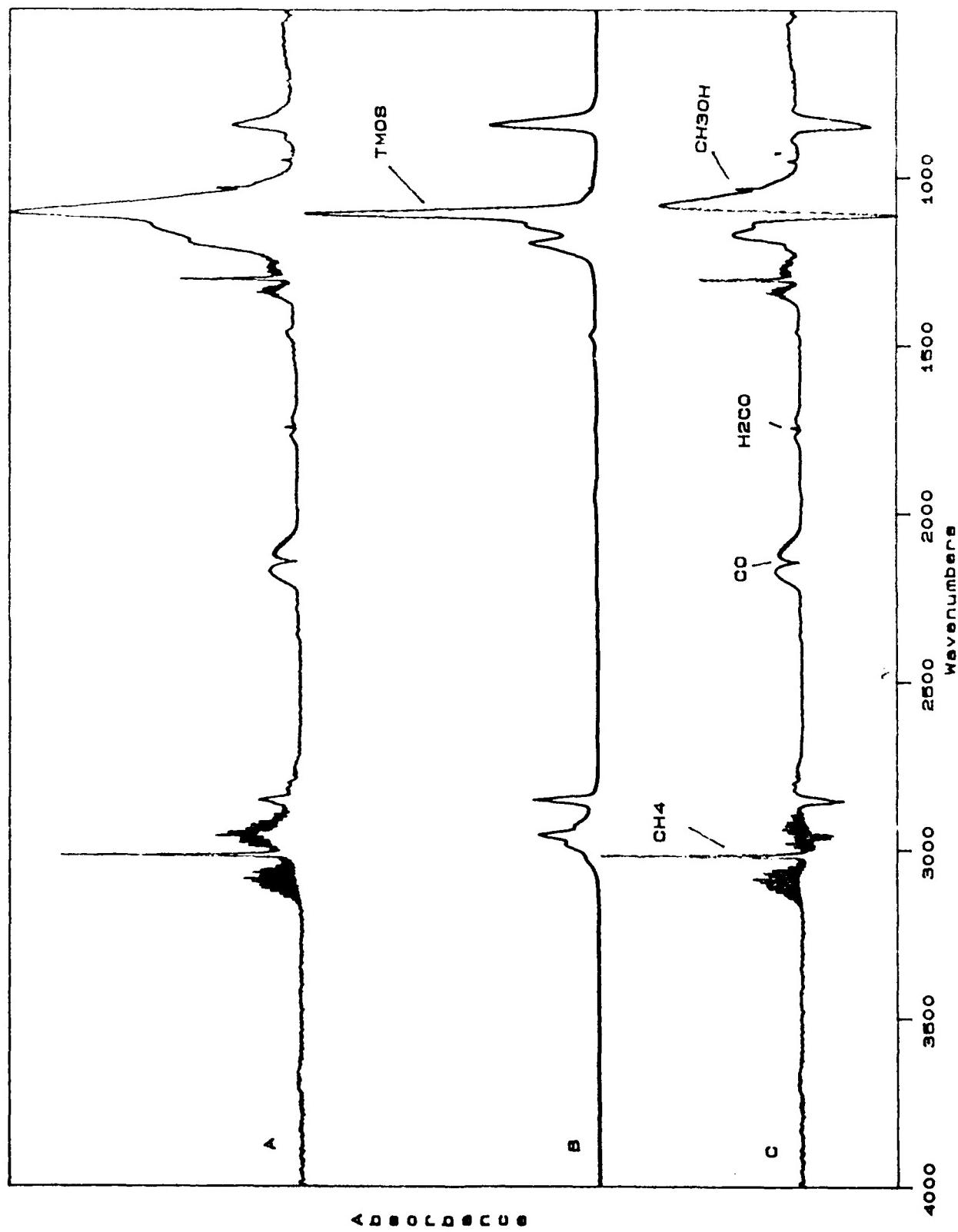
Fig 2. Typical TEOS FTIR spectra from 239 torr samples. (A) 0.1% TEOS/Ar mixture pyrolyzed at  $P=725$  torr,  $T=813$  K for 6 minutes. (B) unpyrolyzed 0.1% TEOS mixture (C) the difference between (A) and (B).

Fig 3. Concentration-time profiles of various species produced during TMOS thermal decomposition.  $P = 704$  torr,  $T= 968$  K, 0.6% TMOS/Ar mixture.

Fig 4. Concentration - time profiles of various species produced during TEOS thermal decomposition.  $P = 755$  torr,  $T=820$  K, 0.06% TEOS/Ar mixture.

Fig 5. Apparent first order decay plots for TMOS at 858 K, 704 torr (triangle) and TEOS at 820 K, 725 torr (square). The Y axis is mole fraction.

Fig 6. Comparison of TMOS (square) and (triangle) global rate constants.



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